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Temperature dependent impedance and dielectric properties of 0.7 $CaTiO_3$-0.3 $NdAlO_3$ ceramics

K Sudheendran & K C James Raju*
School of Physics, University of Hyderabad, Hyderabad 500 046, India

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In this paper, dielectric and impedance spectroscopic studies carried out on a 0.7$CaTiO_3$- 0.3$NdAlO_3$ composition have been reported. The material is synthesized by the conventional ceramic method and the dielectric measurements are carried out as a function of frequency (1 kHz-4.5 MHz) in the temperature range of 150-303 K. The impedance measurement is carried out at different temperatures to separate the grain and grain boundary contributions. The grain boundary resistance is evaluated from the measured *Z-Z"* plots. Both of them are found to be decreasing with the increase in temperature.

For device applications such as microwave dielectric resonators and high-density ceramic capacitors, much attention is paid to dielectric ceramic materials. Due to their high relative permittivity, the alkaline earth titanates with their pervoskite structure have been of great interest to the electronics industry over the past 30 years. Recently, $CaTiO_3$ based dielectric ceramics have been extensively investigated for their microwave dielectric properties. $CaTiO_3$ exhibits a combination of high permittivity (ε_r=170)[1] and modest dielectric loss, which makes it a suitable candidate for various applications. It has been reported that when the alkaline earth titanates were combined with rare earth aluminates it is possible to produce a new class of high Q and temperature stable microwave dielectrics. The rare earth aluminates have got the pervoskite structure with negative temperature coefficient of resonance frequency (τ_f) and high Q values. Whereas, $CaTiO_3$ has got positive τ_f and moderate Q values. So it is possible to tune the τ_f values of $CaTiO_3$ to the single digits by the proper addition of $REAlO_3$ (RE =La, Nd, Sm)[2]. In these series the composition with 0.7$CaTiO_3$-0.3$NdAlO_3$ is found to be having very low loss and relatively high dielectric constant, which makes them suitable for dielectric resonator applications[3,4]. However, the physical properties of the $CaTiO_3$-$NdAlO_3$ dielectric ceramics were not yet fully understood. In this work, dielectric and impedance characteristics of these ceramic systems have been presented. Impedance spectroscopy (IS) has been recognized as a powerful technique to distinguish the grain and grain boundary contribution of many oxide ceramic materials[5,6]. Data from the IS can be analyzed using the different complex formalisms, impedance Z^*, admittance Y^*, permittivity ε^*, and electric modulus M^*, each consists of real and imaginary components, for example, $Z^* = Z' - jZ''$, where Z' and Z'' are the real and imaginary components of the impedance, respectively. The four complex quantities are interrelated, i.e., $M^* = 1/\varepsilon^* = j\omega C_0 Z^* = j\ \omega C_0(1/Y^*)$, where ω is the angular frequency and C_0 is the empty cell capacitance. Data can be presented in complex plain plot. All the formalisms are valuable because of their different dependence with frequency. To identify the grain and grain boundary characteristics, the complex *Z'-Z"* plots are used.

*For correspondence (E-mail: kcjrsp@uohyd.ernet.in)

Experimental Procedure

Samples of (1-x)$CaTiO_3$- x$NdAlO_3$ (x = 0.1, 0.2, 0.3) were prepared by the conventional solid state reaction method from the commercial powders of $CaCO_3$, TiO_2, Nd_2O_3 and Al_2O_3 from Aldrich. The stoichiometric quantity of the powders was homogenized in an agate mortar with acetone as the mixing solvent. After homogenizing the powders were calcined at 1200°C for 2 h. The formation of the compound is confirmed with X-ray diffraction analysis using a Philips powder X ray diffractometer.

For the electrical property measurements, the disks were pressed uniaxially at 6 MPa and were sintered at 1500°C. The disks got densified to 94% of their theoretical value. The micro structural analysis of the polished sintered sample surface was performed with scanning electron microscopy (SEM). The faces of the pellets were applied with silver paints and were annealed at 300°C for 15 min. The impedance measurements were carried out over range of 100 Hz-4 MHz using Agilent 4294A impedance analyzer interfaced with PC in the temperature range of 150-303 K.

Results and Discussion

The X-Ray diffractogram collected from the (1-x) $CaTiO_3$-x$NdAlO_3$ for x= 0.1, 0.2, and 0.3 are given in Fig 1.

The figure shows a complete solid solubility across the entire compositional range. The structure of the perovskite solid solution is found to be exhibiting orthorhombic symmetry similar to that of pure $CaTiO_3$. Microstructure of the sample is shown in Fig. 2.

The grain shape is found to be uniform and cubical and the size fairly uniform in the range of 2-3 μm.

The temperature dependence of the complex impedance plots for the sample is shown in Fig. 3. From the impedance plane plot it is clear that at low temperature there are two distinct parts for the plot. These two distinct parts in the impedance plots represents the grain and grain boundary related mechanisms, which contribute to the total resistance of the sample.

As the temperature increases it can be noticed that the separation is not well versed which means the grain and grain boundary semicircles overlap with each other. This implies that the distribution of the relaxation time constant τ of these two regions falls within the limit of 1 or 1.5τ. The samples used in the present study show the presence of two semicircles, which indicates the presence of two relaxation processes originating from the grain and grain boundary. At the lower temperatures the grain boundaries are exhibiting large resistances compared to the grain part so that the time constant for these two processes are well separated. As the temperature increases both the grain and grain boundary resistance are coming down and that is leading to overlapping of the two semicircles at the high temperature side.

Temperature and frequency dependence of ε' and loss tangent tanδ for the samples are shown in Figs 4-7. The dielectric constant of the sample investigated is found to be decreasing with the increasing frequency and the dielectric loss tangent is found to be increasing with the increasing frequency.

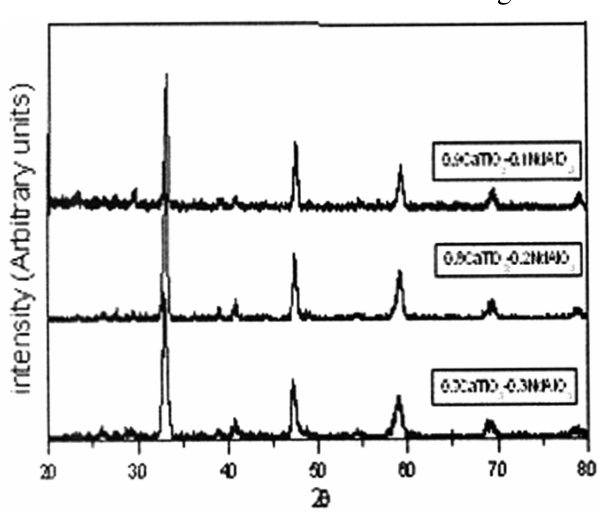

Fig. 1— X-Ray diffraction pattern of the compositions prepared

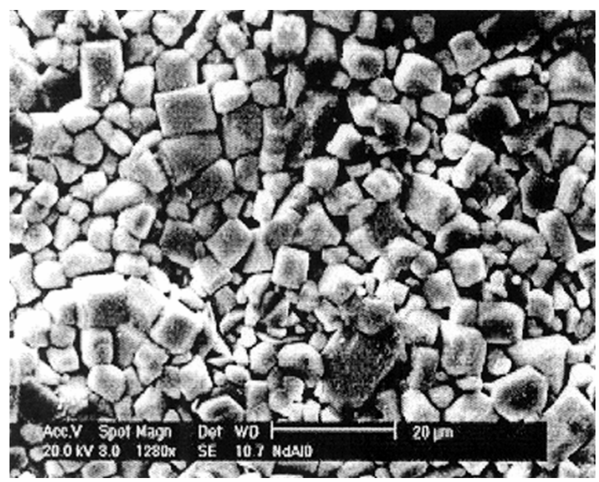

Fig. 2— SEM micrograph of $0.7CaTiO_3$-$0.3NdAl_2O_3$ ceramic

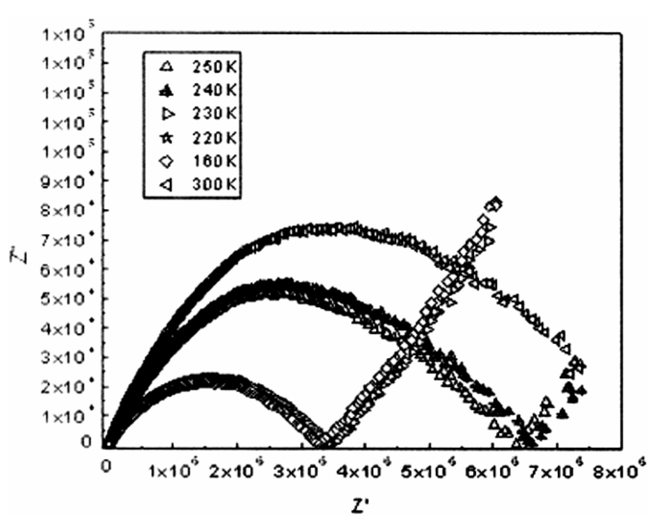

Fig. 3— Temperature dependents Z'-Z" plots for $0.7CaTiO_3$-$0.3NdAlO_3$

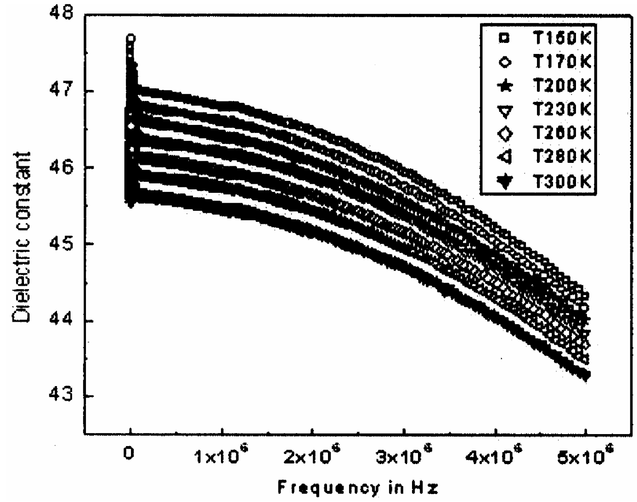

Fig. 4— Frequency dependence of the dielectric constant for $0.7CaTiO_3$-$0.3NdAlO_3$

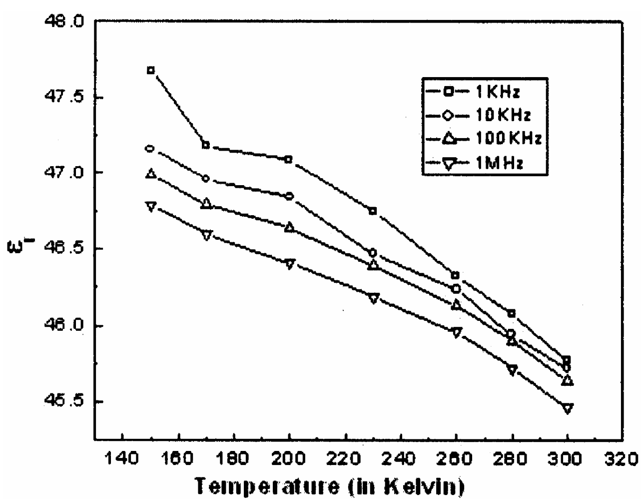

Fig. 5— Temperature dependence of the dielectric constant for $0.7CaTiO_3$-$0.3NdAlO_3$

The decreasing dielectric constant with the increasing frequency can be attributed to the lagging of the dipoles present in the material, which is a typical Debye type behaviour exhibited by most of the dielectric materials. At very low frequencies the dipoles follow the field and we have the dielectric constant ε' approximately equal to ε_s the dielectric constant at quasi static field. The increasing loss tangent with the increasing frequency is also due to the dipolar lagging taking place in the material.

It is observed that the dielectric constant is increasing slightly with the decreasing temperature. The $CaTiO_3$ with pervoskite structure is already known to be exhibiting this type of behaviour.

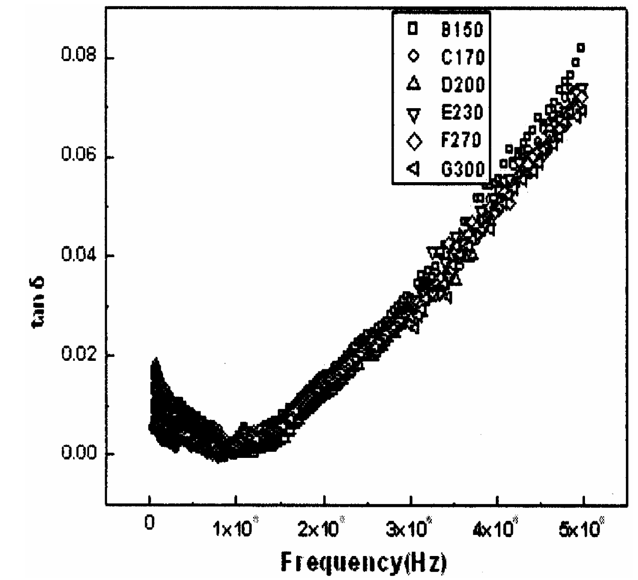

Fig. 6— Frequency dependence of the loss tangent for $0.7CaTiO_3$-$0.3NdAlO_3$

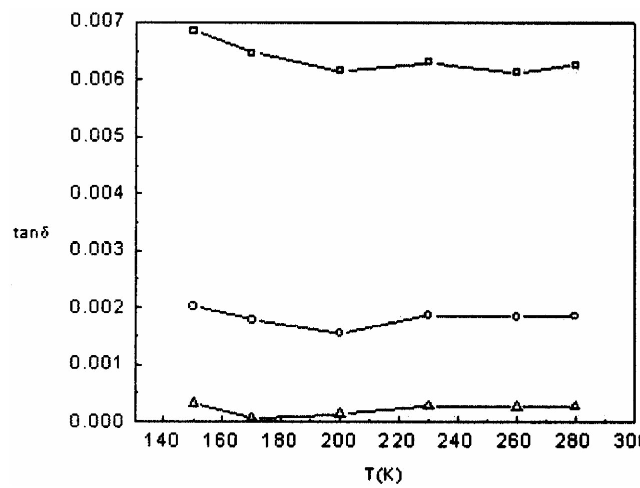

Fig. 7— Temperature dependence of the loss tangent for $0.7CaTiO_3$-$0.3NdAlO_3$

These types of materials are called as incipient ferroelectrics or quantum para electrics. It will have a polar soft mode but they never undergo a phase transition. The observed dielectric behaviour of the $0.7CaTiO_3$-$0.3NdAlO_3$ system suggests that the system is exhibiting incipient ferroelectricity at lower temperatures. The dielectric constant and loss of this composition is found to be much less than that of $CaTiO_3$. This suggest that small amount of $NdAlO_3$ is trying to suppress the incipient ferroelectricity of pure $CaTiO_3$.This suppression of the incipient ferroelectric-city makes them suitable for the dielectric resonator applications.

Conclusions

At the lower temperatures the grain boundaries are exhibiting large resistance compared to the grain part and as the temperature increases both the grain and grain boundary resistance are coming down. The observed dielectric behaviour of the 0.7$CaTiO_3$-0.3$NdAlO_3$ system suggests that it is exhibiting incipient ferroelectricity at lower temperature and its suppression makes them suitable for the dielectric resonator applications when we compare it with $CaTiO_3$.

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